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IV.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE ACTION OF FLUORIDE OF SILICON ON ORGANIC BASES.

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Presented June 15, 1887.

THE research described in the following paper was undertaken in the hope of obtaining from the amines products similar to the compound which ammonia gives with fluoride of silicon, $(NH_3)_2SiF_4$, discovered by Gay-Lussac and Thenard,[*] and three years later prepared and studied by J. Davy.[†] We have been able to find only two previous papers on this subject, one published by Laurent and Delbos,[‡] in 1848, in which the action of fluoride of silicon on aniline is described, the product being a nearly white mass, which they washed with ether, boiled with alcohol, and sublimed to purify it for analysis; their analyses, however, led only to a very complex formula containing oxygen, which they advance "with much reserve," although it was confirmed by the proportions[§] in which its factors combined. The substance when treated with water gave a gelatinous precipitate of silicic acid, and when boiled with alcohol was converted into small white lustrous scales.[‖] The second paper was published by W. Knop,[**] in 1858, and had for its primary object the study of the solution of fluoride of silicon in absolute alcohol, which gave with urea and aniline the fluosilicates of these bases, both of which Knop sublimed, and obtained from the urea fluosilicate only ammonic fluosilicate, silicic acid, and cyanuric acid; but from the aniline fluosilicate a new substance, which gave a precipitate of gelatinous silicic acid with water, and contained more silicon and fluorine than the fluosilicate. He did not, however, identify it with the substance made by Laurent and Delbos. We may add, that some years later W. Knop and W. Wolf* describe the aniline fluosilicate more in detail.

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[*] Mém. d'Arcueil, ii. 317.

[†] Phil. Transact., 1812, p. 352.

[‡] Ann. Chim. Phys., ser. 3, xxii. 101.

[§] These proportions agree tolerably with the formula worked out by us for this substance, but their analytical results do not, and are entitled to no consideration, on account of the difficulties in the analysis, which Laurent and Delbos did not succeed in overcoming.

[‖] Aniline fluosilicate.

[**] Chem. Centralblatt, 1858, p. 388.

The results of our work on this subject may be summarized briefly as follows. Aniline forms with fluoride of silicon a compound having the formula $(C_6H_5NH_2)_3(SiF_4)_2$, which sublimes without alteration, but is decomposed with water forming aniline fluosilicate and silicic acid; when heated with an excess of aniline it is converted into another compound having the formula $(C_6H_5NH_2)_4(SiF_4)_2$, and the same substance is formed when fluoride of silicon acts on aniline at high temperatures. This second product is unstable, breaking up spontaneously into the first and free aniline. The following bases also give compounds containing three molecules of the base to two of fluoride of silicon: paratoluidine, orthotoluidine, parachloraniline, diphenylamine, dimethylaniline, chinoline, and dimethylamine, the last giving also a compound having the formula $((CH_3)_2NH)_4(SiF_4)_2$. On the other hand, we have not succeeded in obtaining from ammonia a compound of the formula $(NH_3)_3(SiF_4)_2$.

We propose to call these substances silicotetrafluorides, a clumsy name, it is true, but one which will designate them with certainty, whereas all the simpler names, such as silicofluoride or fluosilicide, have been used for the fluosilicates at one time or another, and might therefore lead to confusion.

The remainder of the paper contains the detailed account of our experimental results, and at the end a discussion of our views in regard to the constitution of the silicotetrafluorides.

PRODUCTS OF THE ACTION OF FLUORIDE OF SILICON ON ANILINE.

Trianiline Disilicotetrafluoride, $(C_6H_5NH_2)_3(SiF_4)_2$. — This substance was prepared by passing fluoride of silicon over aniline. The fluoride of silicon was made in the usual way, from calcic fluoride, sand, and sulphuric acid; but as we found that a glass flask after using it two or three times became perforated by the small quantities of hydrofluoric acid formed in the process, we replaced it by a thick glass bottle warmed in a water-bath, which lasted through a number of preparations. The delivery-tube should not dip below the surface of the aniline, as in that case there is danger that it will be stopped by the product; but if it is brought near the surface of the base, the action takes place so rapidly that very little of the fluoride of silicon is lost. A good deal of heat is given out during the reaction, and the aniline is converted into a loose white solid, which was washed with hot ligroine until free from aniline, and then its purification finished by two sublimations. The yield was essentially quantitative, 30 grams of aniline giving after treatment with fluoride of silicon for 24 hours 51 grams of product, instead of 52 grams, the amount which should be obtained for the formula* $(C_6H_5NH_2)_3(SiF_4)_2$. The same substance is formed when aniline fluosilicate is sublimed, and the preparation, the analysis of which is numbered I., was made in this way. It is to be observed that the substance analyzed by Laurent and Delbos was really prepared in this way, since by boiling their original product with alcohol they converted it into aniline fluosilicate, which was afterward reconverted into the silicotetrafluoride by sublimation. Also the substance obtained by Knop by sublimation of his aniline fluosilicate was the trianiline disilicotetrafluoride.

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* Chem. Centralblatt, 1862, p. 401.

The method of analysis used for all these substances consisted in neutralizing a weighed quantity of the substance dissolved in hot water in a platinum dish with a standard solution of sodic hydrate, using a solution of litmus as the indicator. The liquid was then heated to boiling, more of the sodic hydrate added, if the reaction had become acid, and evaporated to dryness on the water-bath, the residue treated with water, and the silicic dioxide filtered out. The filtrate, after neutralizing once more with the sodic hydrate, which is usually necessary when the organic base is one with an alkaline reaction, (NH_3 or $(CH_3)_2NH$), is treated with a solution of zincic oxide in ammonic carbonate, evaporated once more to dryness on the water-bath, treated with water, and filtered; the precipitate is dissolved in strong nitric acid, evaporated to dryness, the residue after treatment with strong nitric acid extracted with water, and the silicic dioxide thus obtained added to that from the residue of the first evaporation, ignited, and weighed. The fluorine was usually calculated from the amount of the standard solution of sodic hydrate necessary for the neutralization of the hydrofluoric acid present, but it was also occasionally determined direct in the filtrate from the zincic carbonate and silicate by evaporating to dryness in a platinum crucible, and, after removing any slight excess of sodic carbonate by converting it into acetate and washing with 80% alcohol, igniting and weighing as sodic fluoride.

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* Laurent and Delbos found that 59.5 grm. of aniline absorbed 40.5 grm. of fluoride of silicon. Our formula requires 44.3 grm.

I. 0.2686 grm. of the substance gave 19.6 c.c. of nitrogen at a temperature of 23° and a pressure of 768 mm.
II. 0.2982 grm. of substance gave 0.0751 grm. of silicic dioxide and 0.2105 grm. of sodic fluoride.
III. 0.2842 grm. of substance gave 0.0717 grm. of silicic dioxide and 0.1968 grm. of sodic fluoride.
IV. 0.3784 grm. of substance needed for neutralization 0.2480 grm. of sodic hydrate.

	Calculated for $(C_6H_5NH_2)_3(SiF_4)_2$.	Found. I.	II.	III.	IV.
Nitrogen	8.62	8.31			
Silicon	11.50	. . .	11.75	11.77	
Fluorine	31.24	. . .	31.94	31.33	31.15

Several attempts to make a combustion of the substance have shown that great difficulties stand in the way of getting satisfactory results, and, as the determinations of nitrogen, silicon, and fluorine just given are sufficient to establish its formula beyond a doubt, we have not thought it worth while to devote to the study of the conditions of its combustion the time necessary to obtain an accurate result.

Properties. — The trianiline disilicotetrafluoride is a white semi-crystalline to amorphous solid, which sublimes in the neighborhood of 200° without melting. It is insoluble in ether (anhydrous), benzol, ligroine, chloroform, or carbonic disulphide. It is decomposed very slowly by boiling absolute alcohol without any deposition of silicic acid, and converted into aniline fluosilicate; we have not succeeded in bringing the other product of this reaction into a state fit for analysis; it is a thick liquid, probably a silicic ethylester. The action is more rapid with alcohol containing water. Water decomposes it at once with deposition of silicic acid, and the solution yields on evaporation aniline fluosilicate* in beautiful white pearly scales. Its identity was determined by the following analysis.

0.7488 grm. of substance gave by precipitation with baric chloride 0.6372 grm. of baric fluosilicate.

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* W. Knop and W. Wolf, Chem. Centralblatt, 1862, p. 401.

	Calculated for $(C_6H_5NH_3)_2SiF_6$.	Found.
SiF_6	43.04	43.30

To determine the proportions in which the substances act on each other when water is added to the trianiline disilicotetrafluoride, we have studied the reaction quantitatively with the following results.

1.3092 grm. of the substance were dissolved in water, and the silicic acid precipitated filtered out, ignited, and weighed, giving 0.1200 grm. of silicic dioxide. To the filtrate was added potassic chloride, and the potassic fluosilicate formed was dried at 100° and weighed, giving 0.7370 grm.

These numbers agree best with the following reaction: —

$$4\,(C_6H_5NH_2)_3(SiF_4)_2 + 6\,H_2O = \\ 5\,(C_6H_5NH_3)_2\,SiF_6 + 2\,C_6H_5NH_3F + 3\,SiO_2,^*$$

as is shown by comparing the amounts of the products which would be obtained from 100 grm. of trianiline disilicotetrafluoride according to it, and those which were actually obtained in the experiment just described.

	Calculated from the Reaction.	Found.
Silicic dioxide	9.25	9.17
Aniline fluosilicate	84.70	84.41

Two attempts were made also to determine the amount of aniline fluoride formed (both by titration and by conversion into calcic fluoride) ; but although these experiments proved the presence of a fluoride, they gave results which did not agree with each other or with the theory, the reason being without doubt that a portion of the aniline fluoride was converted into fluosilicate during the filtrations, which we had to carry on in a glass funnel.

The action of ammonia gas upon the trianiline disilicotetrafluoride was studied carefully, since we hoped that it might throw light on the constitution of this substance, and also that the corresponding ammonia compound $(NH_3)_3(SiF_4)_2$ might be formed. Neither of these hopes has been realized, however, for upon passing ammonia gas over the trianiline disilicotetrafluoride the compound was decomposed with a strong evolution of heat, aniline was set free, and the product was the compound of ammonia and fluoride of silicon already described by J. Davy, as was proved by the following analyses, which also show that none of the desired substance $(NH_3)_3(SiF_4)_2$ was formed; and as it was not obtained under these conditions, it is fair to suppose that it cannot exist. The substances for Analyses I. and II. were prepared by washing the aniline out of the crude product of the reaction with ligroine. The substance for Analysis III, was further purified by sublimation.

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* As a matter of fact, it was one of the silicic acids which was precipitated; but as we do not know which one it was, we prefer to write it as silicic dioxide.

I. 0.3414 grm. of the substance gave 0.1496 grm. of silicic dioxide and 0.4154 grm. of sodic fluoride.
II. 0.4400 grm. gave 0.1937 grm. of silicic dioxide.
III. 0.3770 grm. gave 0.1625 grm. of silicic dioxide.
IV. 0.1920 grm. gave 0.0840 grm. of silicic dioxide.

	Calculated for	Found.			
	$(NH_3)_4(SiF_4)_2$.	I.	II.	III.	IV.
Silicon	20.29	20.44	20.55	20.12	20.41
Fluorine	55.07	55.03			

It was noticed during the purification of this substance that it sublimed at a much higher temperature than the trianiline disilicotetrafluoride. The reaction which takes place when trianiline disilicotetrafluoride is treated with ammonia gas is the following:

$$(C_6H_5NH_2)_3(SiF_4)_2 + 4\,NH_3 = (NH_3)_4(SiF_4)_2 + 3\,C_6H_5NH_2,$$

as was proved by its quantitative investigation.

2.8564 grm. of trianiline disilicotetrafluoride yielded after treatment with ammonia 1.6240 grm. of $(NH_3)_4(SiF_4)_2$.

	Calculated Percentage according to the Reaction given above.	Found.
$(NH_3)_4(SiF_4)_2$	56.67	56.85

When hydrochloric acid gas is passed over trianiline disilicotetrafluoride there is no action in the cold; but if the substance is gently warmed, complete decomposition sets in, aniline chloride sublimes along the tube in needles, and the hydrochloric acid contains fluoride of silicon, as was shown by passing it into water when a precipitate of silicic acid was formed.

The action of ethyliodide was also tried. At 100° there was no action, but at 150° a product was formed which contained neither fluorine nor silicon, fluoride of silicon being given off when the tube was opened. Under these circumstances, we did not think it worth while to try to purify the residual substance for analysis. Ethylbromide acted in the same way, but with more difficulty. Strong sulphuric acid decomposes trianiline disilicotetrafluoride, giving off fluoride of silicon. The action of the other common reagents with this substance could not be studied, because it is decomposed by water or alcohol.

Dianiline Silicotetrafluoride, $(C_6H_5NH_2)_4(SiF_4)_2$.— This substance was formed when aniline vapor was conducted into a receiver filled with fluoride of silicon, in the hope of preparing a compound containing a larger proportion of fluoride of silicon than that in the substance just described. The fact that, on the contrary, a body richer in aniline is formed, is probably to be accounted for by the high temperature at which the union of the two substances took place; and this view is confirmed by some experiments in which we heated the trianiline disilicotetrafluoride with one molecule of aniline to 150° in a sealed tube for about five hours: the product was a purplish mass, which gave results on analysis showing that a considerable quantity of aniline had been taken up, although not quite enough to convert the trianiline disilicotetrafluoride completely into the dianiline silicotetrafluoride. As the substance prepared directly from aniline and fluoride of silicon could not be purified on account of its slight stability, it was analyzed in the crude state with the following results, which are as accurate as could be expected under these circumstances.

I. 0.3803 grm. of the substance gave 0.0826 grm. of silicic dioxide and 0.2255 grm. of sodic fluoride.

II. 0.3032 grm. of the substance gave 0.0645 grm. of silicic dioxide and 0.1798 grm. of sodic fluoride.

	Calculated for $(C_6H_5NH_2)_4(SiF_4)_2$.	Found.	
		I.	II.
Silicon	9.65	10.14	9.93
Fluorine	26.20	26.83	26.85

Properties. — It is a white powder which cannot be sublimed, as it decomposes with blackening when heated. With water it is decomposed and dissolved with deposition of silicic acid. It is possessed of but slight stability, as it gradually decomposes spontaneously even when kept in a corked tube at ordinary temperatures, the substance turning yellow and giving up aniline, which was extracted with ligroine, and recognized by its smell and its characteristic color with bleaching-powder, while the residue was pure trianiline disilicotetrafluoride, as shown by the following analyses.

I. 0.2370 grm. of the substance gave 0.0578 grm. of silicic dioxide and 0.1637 grm. of sodic fluoride.

II. 0.1236 grm. of the substance gave 0.0841 grm. of sodic fluoride.

	Calculated for		Found.	
	$(C_6H_5NH_2)_3(SiF_4)_2$.	$(C_6H_5NH_2)_4(SiF_4)_2$.	I.	II.
Silicon	11.50	9.65	11.39	
Fluorine	31.24	26.20	31.25	30.79

In view of this decomposition of the dianiline silicotetrafluoride into aniline and trianiline disilicotetrafluoride, and also of the formation of the dianiline silicotetrafluoride by heating aniline with trianiline disilicotetrafluoride, there seems no doubt that the real formula of this substance is $(C_6H_5NH_2)_4(SiF_4)_2$, that is, double the simplest formula determined by analysis, and that the reaction for its spontaneous decomposition is the following:

$$(C_6H_5NH_2)_4(SiF_4)_2 = C_6H_5NH_2 + (C_6H_5NH_2)_3(SiF_4)_2.$$

ACTION OF FLUORIDE OF SILICON ON OTHER BASES.

Triorthotoluidine Disilicotetrafluoride, $(C_7H_7NH_2)_3(SiF_4)_2$. — This substance was prepared by passing fluoride of silicon into a solution of orthotoluidine in benzol, when a very heavy gelatinous precipitate was formed, which was purified by washing with benzol and three sublimations. It can be formed also by the methods given under the aniline compound, but precipitation from a benzol solution gives the result more easily, and furnishes a purer product. Its composition was determined by the following analyses.

I. 0.2100 grm. of the substance gave 0.0476 grm. of silicic dioxide.

II. 0.3530 grm. of the substance gave 0.2177 grm. of sodic fluoride.

III. 0.2330 grm. of the substance gave 0.1440 grm. of sodic fluoride.

IV. 0.2050 grm. of the substance gave 0.1266 grm. of sodic fluoride.

	Calculated for		Found.		
	$(C_7H_7NH_2)_3(SiF_4)_2$.	I.	II.	III.	IV.
Silicon	10.58	10.58			
Fluorine	28.73	. . .	27.90	27.97	27.94

Properties. — It is a white powder subliming without melting or decomposition, like the corresponding aniline compound. It dissolves in hot common alcohol, and the solution deposits on cooling orthotoluidine fluosilicate in fine needles.

Triparatoluidine Disilicotetrafluoride $(C_7H_7NH_2)_3(SiF_4)_2$. — This substance was made and purified like the corresponding ortho compound, that is, by passing fluoride of silicon through a solution of paratoluidine in benzol, but even after four sublimations it had a distinct yellowish color; that the substance is essentially pure, however, in spite of this coloration, is shown by the following analyses.

I. 0.1928 grm. of the substance gave 0.0438 grm. of silicic dioxide.
II. 0.1472 grm. of the substance gave 0.0922 grm. of sodic fluoride.

	Calculated for $(C_7H_7NH_2)_3(SiF_4)_2$.	Found.	
		I.	II.
Silicon	10.58	10.60	
Fluorine	28.73	. . .	28.34

In properties it resembles the corresponding ortho compound, but is decidedly less stable, showing a strong tendency to turn yellow on standing, and the paratoluidine fluosilicate deposited, as the hot solution of the substance in alcohol cools, crystallizes in thick needles.

Trimonochloraniline Disilicotetrafluoride, $(C_6H_4ClNH_2)_3(SiF_4)_2$. — This substance was made by passing fluoride of silicon over parachloraniline, and was purified by sublimation. Its composition was determined by the following analysis.

0.4807 grm. of the substance gave 0.0990 grm. of silicic dioxide, and 0.2686 grm. of sodic fluoride.

	Calculated for $(C_6H_4ClNH_2)_3(SiF_4)_2$.	Found.
Silicon	9.48	9.61
Fluorine	25.75	25.29

It resembles the corresponding aniline compound in its properties, and forms with hot alcohol a solution of the parachloraniline fluosilicate, which separates as the solution cools in beautiful long slender needles.

Parabromaniline forms a similar compound with fluoride of silicon, and gives with hot alcohol a solution depositing the parabromaniline fluosilicate in small pearly scales.

With *symmetrical tribromaniline* we could get no action, when we treated it with fluoride of silicon, the result of the experiment being negative, whether it was acted on alone in the solid state, or fused, or in solution in benzol. Symmetrical tribromaniline therefore does not combine with fluoride of silicon under the conditions which bring about the union with it of all the other bases studied.

Tridiphenylamine Disilicotetrafluoride, $((C_6H_5)_2NH)_3(SiF_4)_2$. — Solid pure diphenylamine is not acted on by fluoride of silicon; the statement made in a preliminary notice of this work, that a compound was formed under these conditions was incorrect, the diphenylamine used for that first experiment being impure. If, however, fluoride of silicon is passed through a solution of diphenylamine in benzol, a white crystalline precipitate is deposited slowly, which was washed with benzol, dried at 100°, and analyzed with the following results.

I. 0.4356 grm. of the substance gave 0.0695 grm. of silicic dioxide and 0.2141 grm. of sodic fluoride.
II. 0.4192 grm. of the substance gave 0.1986 grm. of sodic fluoride.

	Calculated for $((C_6H_5)_2NH)_3(SiF_4)_2$.	Found.	
		I.	II.
Silicon	7.83	7.44	
Fluorine	21.26	22.23	21.43

Properties. — It forms thick white needles, which are decomposed by heat into fluoride of silicon and diphenylamine. When treated with water a precipitate of diphenylamine separates, and the filtrate contains fluosilicic acid. A quantitative study of the reaction gave the following results.

I. 0.8135 grm. of the substance gave 0.5686 grm. of diphenylamine and 0.3040 grm. of potassic fluosilicate.
II. 0.4934 grm. of the substance gave 0.3476 grm. of diphenylamine.

In the calculated percentages given below, it is assumed that all the diphenylamine is separated by the action of the water, and that four molecules of the compound will yield five of potassic fluosilicate, i. e. that the reaction with water is analogous to that of the corresponding aniline compound.

	Calculated.	Found.	
		I.	II.
Diphenylamine	70.91	69.89	70.44
Potassic fluosilicate	38.50	37.37	

If, as the numbers obtained seem to show, the reaction is similar to that of the trianiline disilicotetrafluoride with water, silicic acid should have been set free; but no trace of it could be discovered, the solution being free from any precipitate except the diphenylamine, and upon evaporation to dryness leaving no residue, while that silicic acid had not been carried down by the diphenylamine was shown by burning it, and also by dissolving it in benzol. In neither case did it leave a residue. We have not been able to find any explanation for this curious observation, or to account for the formation of fluosilicic acid without the formation of silicic acid at the same time. That the soluble product was principally fluosilicic acid is proved by the fact that it gave a precipitate with potassic chloride.

Tridimethylaniline Disilicotetrafluoride, $(C_6H_5N(CH_3)_2)_3(SiF_4)_2$.— Fluoride of silicon has no action on dimethylaniline alone, but, if the gas is passed through a solution of dimethylaniline in benzol, a flocculent precipitate is formed, which is gradually converted into a gummy mass that crystallizes on standing. The crystals were purified by washing with benzol and ligroine, dried at 100°, and analyzed.

0.1066 grm. of the substance gave 0.0220 grm. of silicic dioxide and 0.0584 grm. of sodic fluoride.

	Calculated for $(C_6H_5N(CH_3)_2)_3(SiF_4)_2$.	Found.
Silicon	9.81	9.63
Fluorine	26.62	24.77

The number for the fluorine is far from satisfactory, which is accounted for by the difficulty of purifying this decidedly unmanageable substance. It is, however, near enough to show that the substance can have no other composition than that assigned to it by us.

Properties. — It forms an indistinct crystalline mass, which is decomposed by heat, and gives no stable fluosilicate, when treated with alcohol.

Trichinoline Disilicotetrafluoride, $(C_9H_7N)_3(SiF_4)_2$. — Chinoline alone is not acted on by fluoride of silicon; but, if the gas is passed through a solution of chinoline in benzol, a gummy precipitate is formed at first, which becomes gradually converted into needle-shaped crystals. The product was purified by washing with benzol or ligroine, and dried at 100°. The same substance is obtained when chinoline fluosilicate is sublimed, and the analysis numbered II. is of a preparation made in this way.

I. 0.1634 grm. of the substance gave 0.0323 grm. of silicic dioxide.
II. 0.0730 grm. of the substance gave 0.0404 grm. of sodic fluoride.

	Calculated for	Found.	
	$(C_9H_7N)_3(SiF_4)_2$.	I.	II.
Silicon	9.41	9.23	
Fluorine	25.55	. . .	25.01

Properties. — It crystallizes in needles, and sublimes without melting, or decomposition. Although hot alcohol usually decomposes it, as described below, on one occasion it dissolved it without decomposition, and this solution gave on cooling thick needles, which gave the following results on analysis.

0.0903 grm. of the substance gave 0.0176 grm. of silicic dioxide and 0.0506 grm. of sodic fluoride.

	Calculated for $(C_9H_7N)_3(SiF_4)_2$.	Found.
Silicon	9.41	9.10
Fluorine	25.55	25.38

On addition of water the substance analyzed was decomposed with deposition of silicic acid. We have not succeeded, however, in repeating this experiment, as in all other cases the product from the action of hot alcohol has been chinoline fluosilicate, which crystallizes in long thick needles, as the solution cools, and gives a clear solution with water. Its composition was determined by the following analyses of the substance purified by two crystallizations.

I. 0.1244 grm. of the substance gave 0.0200 grm. of silicic dioxide.
II. 0.2054 grm. of the substance gave 0.0325 grm. of silicic dioxide and 0.1254 grm. of sodic fluoride.

	Calculated for	Found.	
	$(C_9H_7N)_2H_2SiF_6$.	I.	II.
Silicon	6.96	7.50	7.38
Fluorine	28.35	. . .	27.64

The trichinoline disilicotetrafluoride resembles the corresponding aniline compound closely in its properties.

Didimethylamine Silicotetrafluoride, $((CH_3)_2NH)_4(SiF_4)_2$. — When dry dimethylamine (prepared according to Baeyer and Caro) was mixed with fluoride of silicon, a white powder was deposited, which was analyzed in the crude state, since it could not be purified because of its very slight stability.

0.2320 grm. of the substance gave 0.0740 grm. of silicic dioxide and 0.2038 grm. of sodic fluoride.

	Calculated for $((CH_3)_2NH)_4(SiF_4)_2$.	Found.
Silicon	14.43	14.89
Fluorine	39.17	39.75

Properties. — A white solid, which like the corresponding compound of aniline is very unstable, decomposing spontaneously at ordinary temperatures into dimethylamine and the following compound, — a decomposition which is hastened by heat.

Tridimethylamine Disilicotetrafluoride, $((CH_3)_2NH)_3(SiF_4)_2$.— This substance was made by subliming the compound just described, when dimethylamine was given off as a secondary product. It was purified by a second sublimation, and its composition determined by the following analyses.

I. 0.1871 grm. of the substance gave 0.0660 grm. of silicic dioxide.
II. 0.2800 grm. of the substance gave 0.0960 grm. of silicic dioxide and 0.2694 grm. of sodic fluoride.

	Calculated for $((CH_3)_2NH)_3(SiF_4)_2$.	Found I.	Found II.
Silicon	16.33	16.46	16.00
Fluorine	44.31	. . .	43.53

Properties. — It is a white powder resembling the corresponding aniline compound in appearance and behavior when heated, although it sublimes at a higher temperature. It also differs from the aniline compound in being deliquescent.

Finally, we may add the following experiments, which gave products of so little promise that we did not attempt to analyze them, but which show that fluoride of silicon acts also on alkaloids, and on amides which can form salts.

Furfurine, when treated in benzol solution with fluoride of silicon, gave a gummy mass similar to that obtained from dimethylaniline, which however did not crystallize on standing.

Dry powdered *urea* was converted by fluoride of silicon into a pasty mass, which was decomposed with evolution of ammonia, when the attempt was made to sublime it. The sublimate contained fluorine and silicon, but we did not continue the study of it, as we had no guaranty that it was a homogeneous substance.

CONSTITUTION OF THE SILICOTETRAFLUORIDES.

Although we have not succeeded in obtaining an absolute direct proof of the constitution of the substances described in this paper, we have been able to reduce the possible formulas that can be assigned to them to a very small number by the following course of reasoning. In the first place, we assume that all the substances described in this paper, which contain three molecules of the base combined with two of fluoride of silicon, have the same constitution, an assumption which is justified by the fact that they are all made by the direct addition of fluoride of silicon to the base, and also by the strong resemblance in their properties, the differences observed being such as might well occur among substances belonging to the same class.

Upon considering, in general, the way in which the fluoride of silicon could attach itself to a base, we have been able to find only three probable methods, which we will proceed to discuss as applied to our compounds. (*a.*) By replacing the hydrogen of the amido group, forming a substance which would be at once an anilid and a fluosilicate. This method would seem at first sight the most probable, especially since A. Harden* has found that chloride of silicon gives with aniline $SiCl_2(NHC_6H_5)_2$ and aniline chloride; but this mode of union is impossible, since both chinoline and dimethylaniline, which contain no hydrogen attached to their nitrogen, form compounds of this class. (*b.*) By the action of the fluoride of silicon on the benzol ring, forming a substance analogous to pararosaniline fluosilicate. This hypothesis, which is improbable on account of the ease with which the substances are broken up by water, is rendered entirely inadmissible by the formation of the dimethylamine compound, which contains no ring. (*c.*) On the supposition that the fluoride of silicon combines with the base to form a sort of salt, this view is the only one compatible with our results, and its correctness is confirmed by the observation that all the substances tried formed salts with one exception, tribromaniline, and that this was the only one which did not form a silicotetrafluoride; further, the stability of the silicotetrafluorides keeps pace with the stability of the salts of the bases, those like aniline, the two toluidines, parachloraniline, chinoline, and dimethylamine, which form stable salts, giving silicotetrafluorides, which can be sublimed without decomposition, whereas diphenylamine and dimethylaniline gave compounds decomposed by heat. That the salts of diphenylamine are unstable, being decomposed by water, is well known, and although we have not been able to find any published statement about the salts of dimethylaniline that would imply they are unstable, our own work has furnished the proof that the fluosilicate at least is less stable than that of aniline, as only the products of the decomposition of the fluosilicate were obtained, when water was added to the tridimethylaniline disilicotetrafluoride.

We infer, then, from the arguments given above, that the nitrogen in the silicotetrafluorides is in the quinquivalent condition, and think it most probable that one of the two additional bonds is satisfied by silicon, the other by fluorine, and that the following graphic formula represents its constitution. It should be remembered, however, that this formula is only the most probable one, for, as already stated, we have been able to bring no absolute proof of its correctness.

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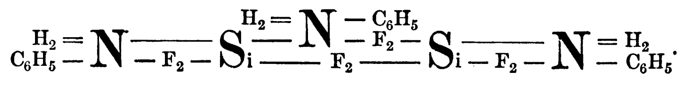
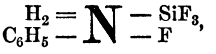
* J. Lond. Chem. Soc., 1887, i. 40.



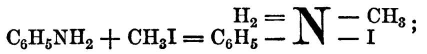
$$\begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}\text{———}\\-F_2-\end{matrix}\mathrm{Si}\begin{matrix}\begin{matrix}H_2=&&-C_6H_5\\-&\mathrm{N}&-F_2-\end{matrix}\\\text{——}\ F_2\ \text{——}\end{matrix}\mathrm{Si}\begin{matrix}\text{———}\\-F_2-\end{matrix}\mathrm{N}\begin{matrix}=H_2\\-C_6H_5\end{matrix}.$$

If this formula is adopted, the formation of the silicotetrafluorides can be explained in the following way. In the first place one molecule of the fluoride of silicon acts upon one molecule of the base to give the group

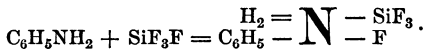


$$\begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}-SiF_3,\\-F\end{matrix}$$

and, although this mode of union seems strange at first sight, it is not without analogy, if we consider the close relationship of silicon and carbon, as then it is similar to the formation of ammonium salts by the action of methyliodide on a base, as shown by the following reactions:

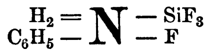


$$C_6H_5NH_2 + CH_3I = \begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}-CH_3;\\-I\end{matrix}$$



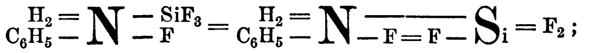
$$C_6H_5NH_2 + SiF_3F = \begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}-SiF_3.\\-F\end{matrix}$$

Since the group

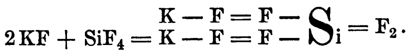


$$\begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}-SiF_3\\-F\end{matrix}$$

is at once a fluoride and a substituted fluoride of silicon, an action next takes place similar to the formation of a fluosilicate from a fluoride and fluoride of silicon, thus:



$$\begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}-SiF_3\\-F\end{matrix}=\begin{matrix}H_2=\\C_6H_5-\end{matrix}\mathrm{N}\begin{matrix}\text{————}\\-F=F-\end{matrix}\mathrm{Si}=F_2;$$



$$2KF + SiF_4 = \begin{matrix}K-F=F-\\K-F=F-\end{matrix}\mathrm{Si}=F_2.$$

In this reaction the formation is assumed of the bivalent radical F_2^{II}, which has been proved to exist in hydrofluoric acid by Mallet's determination* of the vapor-density leading to the formula H_2F_2, and the assumption of the presence of which in fluosilicic acid explains its relation to silicic acid in the most satisfactory way. The substance

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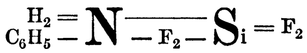
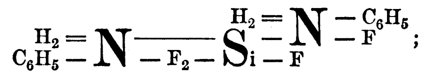
* Am. Chem. J., iii. 189.



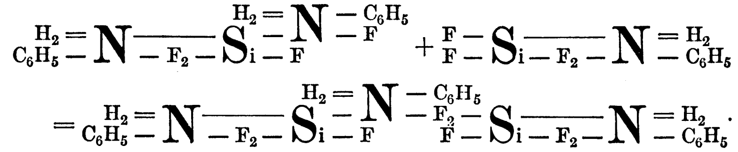
$$\begin{array}{r}H_2=\\C_6H_5-\end{array}\mathrm{N}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{Si}=F_2$$

next acts on another molecule of the base in the same way that the fluoride of silicon did originally, forming



$$\begin{array}{r}H_2=\\C_6H_5-\end{array}\mathrm{N}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{Si}\begin{array}{l}-\overset{H_2=}{}\mathrm{N}\begin{array}{l}-C_6H_5\\-F\end{array}\\-F\end{array};$$

but it would seem that the acid nature of the silicon has been so weakened by the introduction of two aniline molecules, that the atom of fluorine left attached to the silicon cannot combine with the fluorine attached to the nitrogen, and therefore this latter is saturated by the more acid fluorine of a fluoride of silicon carrying only one aniline molecule, thus:

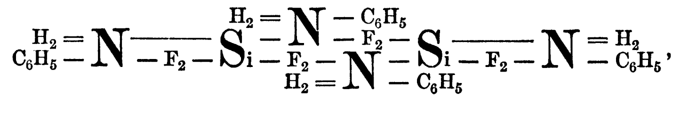


$$\begin{array}{r}H_2=\\C_6H_5-\end{array}\mathrm{N}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{Si}\begin{array}{l}-\overset{H_2=}{}\mathrm{N}\begin{array}{l}-C_6H_5\\-F\end{array}\\-F\end{array}+\begin{array}{r}F-\\F-\end{array}\mathrm{Si}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{N}\begin{array}{l}=H_2\\-C_6H_5\end{array}$$

$$=\begin{array}{r}H_2=\\C_6H_5-\end{array}\mathrm{N}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{Si}\begin{array}{l}-\overset{H_2=}{}\mathrm{N}\begin{array}{l}-C_6H_5\\-F_2-\end{array}\\-F\qquad F-\end{array}\mathrm{Si}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{N}\begin{array}{l}=H_2\\-C_6H_5\end{array}.$$

If then the two atoms of fluorine remaining attached simply to silicon are united, the formula given above is constructed. Our only reason for joining these last atoms of fluorine is that it makes the molecule more symmetrical, but it is also possible that they remain univalent.

Turning next to the compounds formed by the union of the base and fluoride of silicon in the proportion of two molecules of the former to one of the latter; as has been already argued, it is necessary to double the simplest formula which can be assigned to these substances, because they break up into the free base and the compound of three molecules of the base to two of fluoride of silicon, and also because they can be formed by a reaction the reverse of this decomposition. If, then, the formula discussed above is given to the trianiline disilicotetrafluoride, the formula of the dianiline silicotetrafluoride must be



$$\begin{array}{r}H_2=\\C_6H_5-\end{array}\mathrm{N}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{Si}\begin{array}{l}-\overset{H_2=}{}\mathrm{N}\begin{array}{l}-C_6H_5\\-F_2-\end{array}\\-F_2-\underset{H_2=}{}\mathrm{N}-C_6H_5\end{array}\mathrm{Si}\begin{array}{c}\rule{2em}{0.4pt}\\-F_2-\end{array}\mathrm{N}\begin{array}{l}=H_2\\-C_6H_5\end{array},$$

and the very slight stability of the substance can be explained by the neutralization of the acid properties of the silicon and fluorine, already alluded to, by the introduction of so many molecules of base, which makes them hold the last molecule of the base with comparatively little force. On the other hand, we have not been able to find any explanation for the stability of the compound derived from ammonia, as the only one we could think of — viz. that the ammonia being a stronger base than aniline would attach itself more firmly to the slightly acid molecule — is rendered inadmissible by the slight stability of the compound made from dimethylamine, a base nearly, if not quite, as strong as ammonia itself. It is possible that the ammonia compound has an entirely different constitution from the compounds of the organic bases, but we have no experimental material for testing the correctness of this hypothesis except Mixter's determination * of the vapor density of this substance, which showed that it was dissociated into four volumes of ammonia and two of fluoride of silicon, and therefore that the simplest formula of the ammonia compound must be doubled, which would look as if it had a constitution similar to the organic compounds.

We may add that Harden † obtained by the action of chloride of silicon on pyridine, or chinoline compounds $(C_5H_5N)_2SiCl_4$, and $(C_9H_7N)_2SiCl_4$; but as they give up chloride of silicon spontaneously, it is probable that they are not analogous in constitution to our substances.

The study of the action of fluoride of silicon on organic bases will be continued by one of us in this Laboratory.

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* Am. Chem. J., ii. 153.

† J. Lond. Chem. Soc., 1887, i. 40.